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(54) **Nitrided stainless steel.**

(57) Nitrided stainless steel comprises austenitic stainless steel wherein a portion of the surface layer at least is composed of a nitrided hard layer which
(A) contains substantially no crystalline chrome nitride;
(B) contains N atoms at 2 to 12% by weight in the base phase austenitic stainless steel phase of base phase.
Such nitrided stainless steel has excellent anti-corrosion properties and surface hardness. There is no dimensional change or surface roughness caused by deposition of crystalline chrome nitride, and so no final finishing process is required.

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This invention relates to nitrided stainless steel products superior both in anti-corrosion property and surface hardness.

Generally, austenitic stainless steel products such as screws have been widely employed because of their superiority in not only corrosion resistance, but also toughness, workability, heat resistance and non-magnetic property and the like. However, although austenitic stainless steel products have excellent anti-corrosion property, as mentioned above, they do not have quenching hardenability so that they are not suitable for such usage as requires high surface hardness.

Among stainless steel materials, martensitic stainless steel containing chrome at 13 to 18% (by weight; the same applies hereinafter) have been also employed besides the above austenitic stainless steel. This martensitic stainless steel has quenching hardenability, however, it is inferior greatly in its corrosion resistance property to austenitic stainless steel. Therefore, this material cannot be applied to the such usage as requires corrosion resistance. On the other hand, from the viewpoint that the above austenitic stainless steel lacks surface hardness, hard chrome plating and the like has been applied in order to improve the deficiency. However, there is a problem practically in the above plating because the adhesion of plating coat is low thereto.

Recently, corrosion resistance of stainless steel has been focused on. It has been increasingly demanded to maintain this corrosion resistance and at the same time to improve its surface hardness. For this purpose, it has been attempted to apply nitriding treatment to austenitic stainless steel superior in corrosion resistance (18-8 stainless steel containing 18% chrome and 8% nickel has been widely employed) and to form a nitrided hard layer so as to improve its surface hardness.

As a method of nitriding treatment, a variety of methods such as salt bath nitriding treatment, ionitriding treatment, gas nitriding and the like are available. Nitriding temperature is usually set around 550 to 570 °C, and around 480 °C at the lowest in these nitriding treatments. As results of nitriding screws made of austenitic stainless steel by such nitriding methods, in spite that the surface hardness has been improved, original property of corrosion resistance for stainless steel deteriorates so that a defect of easily rusting has been caused.

It has been desired to provide stainless steel products which have both high anti-corrosion property and superior surface hardness.

The base material of stainless steel products of the present invention comprises austenitic stainless steel wherein a portion of the surface layer at least is composed of a nitrided hard layer being in accord with the following (A) and (B):

(A) such a nitrided hard layer contains substantially no crystalline chrome nitride ;

(B) such a nitrided hard layer as contains N atoms at 2 to 12% in austenitic stainless steel phase of base phase.

Preferably the nitrided hard layer contains 2 to 5% N by weight N atoms.

A series of studies has been made to pursue a cause of deteriorating corrosion resistance property by the above nitriding treatment. As a result, it has been found that the above deterioration of corrosion resistance was caused because crystalline chrome nitride (CrN) was produced by deposition in the formed nitrided layer and then the concentration of solid soluble chrome (Cr) in the basic phase (austenitic phase) sharply decreases, wherein active chrome indispensable to form a passive layer coat almost disappears, for the passive layer coat functions as retaining corrosion resistance property, original property for stainless steel. And as results of further accumulated researches, the following are found. When the above nitriding treatment for austenitic stainless steel was set considerably at a low temperature (in the lower range by 100 to 200 °C than prior nitriding temperature 480 to 580 °C), N atoms can penetrate the base phase (γ phase) of austenitic stainless steel without depositing solid soluble chrome nitride (CrN) or iron nitride and then that corrosion resistance does not deteriorate by limiting the amount of the above penetration (amount of content) within 2 to 12%, and further a nitrided hard layer having superior surface hardness can be formed by the above penetration of N atoms. It is thought that the above N atoms only penetrate γ phase in this case and the lattice is distorted thereby, however, deposition of crystalline chrome nitride and the like is not led. When the volume of containing the above N atoms is over the above upper limitation, corrosion resistance property may deteriorate because crystalline chrome nitride may be produced by N atoms, which penetrate thereto, and chrome. Meanwhile, when it is below the above lower limitation, a nitrided hard layer having surface hardness cannot be adequately produced.

It is confirmed by an X-ray diffraction method that stainless steel product of the present invention contains substantially no crystalline chrome nitride as the above mentioned and that the amount of N atoms contained in the austenitic stainless steel phase can be identified by ESCA (Electron Spectroscopy for Chemical Analysis) or EPMA (Electron Probe Micro Analyzer). In this case, "contains substantially no crystalline chrome nitride" means that the content is a very small amount (not more than 5%).

The present invention is now described in further detail.

Nitrided stainless steel products of the present invention can be obtained by nitriding austenitic stainless steel itself as a raw material, or nitriding an austenitic stainless steel product which is formed into a defined shape. As the above austenitic stainless steel materials, a variety of austenitic stainless steel varied in elements and ingredients can be available in accordance with the characteristic required such as corrosion resistance, processing hardenability, heat resistance, machinability, non-magnetic property and the like, based upon 18-8 austenitic stainless steel as mentioned above. In addition, Cr-Ni-Mo austenitic stainless steel containing not less than 22% chrome is suitable. Still furthermore, austenitic stainless steel having chrome less than 22% but molybdenum not less than 1.5% is suitable.

The nitriding treatment for the above austenitic stainless steel or its formed products (these are called as stainless steel products) is performed in the following method. That is, prior to nitriding treatment, fluoriding treatment is performed to promote the penetration of N atoms in nitriding treatment. As fluoride-containing gases to fluoride, fluorine compound gas such as NF_3, BF_3, CF_4, HF, SF_6, C_2F_6, WF_6, CHF_3, or SiF_4 are used independently or in combination. Besides, fluorine compound gas with F in its molecule can be used as the above-mentioned fluorine- or fluoride-containing gas. This fluorine- or fluoride-containing gas can be used independently, but generally is diluted by inert gas such as N_2 gas for the treatment. The concentration of the fluorine- or fluoride-containing gas itself in such a diluted gas should amount to, for example, 10,000 to 100,000ppm, preferably 20,000 to 70,000ppm, more preferably 30,000 to 50,000ppm. In the light of practicability, NF_3 is the best among the above compound gases. This is because NF_3 has chemical stability and is easy to treat since it is in a state of gas at normal temperature.

First of all, a fluorine- or fluoride-containing gas atmosphere is prepared at the above-mentioned concentration, wherein the above stainless steel product is held in a heated condition. In this case, stainless steel product itself is heated up to the temperature of 300 to 550 °C. The holding time of the above-mentioned stainless steel product in a fluorine- or fluoride-containing gas atmosphere may appropriately be selected depending on geometry, dimension and the like, generally within the range of ten or so minutes to several hours or scores of minutes. Such a fluoriding treatment allows "N" atoms to penetrate into the surface layer of stainless steel products. Though its mechanism has not been proven at present yet, it can be understood as follows on the whole. That is, a passive layer coat is formed, which inhibits penetration or diffusion of N atoms as a function of nitriding, on the surface of the above stainless steel product. Therefore, according to the prior method, N atoms could not penetrate thereto due to the presence of passive layer coat (oxidized layer) unless temperature for nitriding treatment is set at high temperature. As a result, crystalline chrome nitride is deposited in the surface hard layer. However, fluoriding treatment is performed under fluorine- or fluoride- containing gas atmosphere prior to the nitriding treatment in the present invention. Upon holding the stainless steel product having an oxidized layer in a fluorine- or fluoride-containing gas atmosphere like the above with heating, the passive coat layer is converted to a fluorinated layer. Since "N" atoms for nitrization penetrate more readily into the fluorinated layer than into the passive coat layer, the surface of the above stainless steel product is formed on the suitable condition for penetration of "N" atoms by the above-mentioned fluorination. Thus, it is considered that "N" atoms in the nitriding gas penetrate uniformly into the surface of the stainless steel product to a certain depth when the stainless steel product is held in a nitriding atmosphere with suitable surface condition to absorb "N" atoms, shown below, resulting the formation of a deep uniform nitriding layer.

Thus, the stainless steel product with suitable surface condition to absorb "N" atoms by fluorination is held with heating in a nitriding atmosphere to nitride. In this case, nitriding gas composing a nitriding atmosphere is a simple gas composed of NH_3 only, or a mixed gas (for example, NH_3, CO and CO_2) composed of carbon source gas (for example, RX gas) with a mixed gas composed of NH_3 . Generally, the above-mentioned simple gas or gas mixture is used by mixing an inert gas such as N_2. According to the case, H_2 gas is further added to those gases . In such a nitriding atmosphere, the above-mentioned fluorinated stainless steel product is held with heating. In this case, a heating condition is set at a temperature not more than 450 °C, which is greatly lower than that in the prior method. Especially, the preferable temperature is between 370 and 420 °C. When the above temperature is over 450 °C crystalline CrN is formed in a nitrided hard layer and concentration of active chrome in the base phase decreases, and then as a result anti-corrosion property of stainless steel deteriorates. Furthermore, nitriding treatment at not more than 420 °C is preferable because superior anti-corrosion property is realized as same degree as that of austenitic stainless steel itself and also, a nitrided hard layer greatly superior in hardness can be formed on the surface of stainless steel products. On the other hand, nitriding treatment at not more than 370 °C only realizes a nitrided hard layer not more than 10 μm in depth, even if nitriding treatment time is set at 24 hours, which is of little industrial value and not practical. Generally, the above nitriding treatment time is set within the range of 10 to 20 hours.

By this nitriding treatment, a close nitriding layer of about 20 to 40 μm, (consisting of entirely single layer) is formed uniformly on the surface of the above-mentioned stainless steel product. According to the above nitriding treatment, dimensional change and surface roughness are hardly caused on austenitic stainless steel products. That is, in the prior method, the frame of a stainless steel product may be expanded and then dimensional change may be caused due to deposition of crystalline chrome nitride and the like, and also surface roughness may be deteriorated so that it requires a great amount of cost for final finishing, and furthermore, it is difficult for the technique to be applied to precision machines. On the other hand, the nitrided hard layer in the present invention contains substantially no crystalline chrome nitride and is composed of close organization, so that dimensional change or deterioration of surface roughness may not be caused and as a result it does not require the final processing for finishing.

The crystalline chrome nitride is not contained in this nitrided hard layer while "N" atoms is contained in austenitic phase of base phase (γ phase) at the rate of 2 to 12%. Therefore, the stainless steel products in which the nitriding treatment is given (that is to say, the nitrided stainless steel products) has corrosion resistance property as high as the austenitic stainless steel in which the nitriding treatment is not given and furthermore, the surface hardness is greatly improved thanks to the presence of the above nitrided hard layer. The superior the corrosion resistance property of such nitrided stainless steel products is, the lower the processing hardness is or the more precisely the surface condition before being nitrided is polished. In addition, from the viewpoint of materials, the more chrome is contained thereto such as SUS310 (chrome: 25%, nickel: 20%), the better corrosion resistance is. Furthermore, regarding 18-8 austenitic stainless steel materials, the more molybdenum is contained thereto, the better it is. The nitrided stainless steel products obtained in the above method have corrosion resistance property as same as the austenitic stainless steel before being nitrided, besides the surface hardness is greatly improved and still moreover it becomes non-magnetic. Namely, according to the conventional nitriding method, the non-magnetic property is deteriorated, which originally belongs to austenitic stainless steel itself, by deposition of crystalline chrome nitride and then the nitrided hard layer takes on the character of magnetic property. Meanwhile, since the nitrided hard layer in the present invention contains substantially no crystalline chrome nitride, the non-magnetic property is maintained. Therefore, it is suitable for the usage which requires non-magnetic property such as products in relation to computer.

Furthermore, it is possible that treatment by strong mixed acid containing HNO_3 is performed on the above stainless steel products after being nitrided. The oxidized scale attached to the surface of stainless steel products after being nitrided can be removed by this treatment, and at the same time, according to the case, a passive layer (an oxidized layer), caused by the solid soluble chrome, can be formed thickly at the early stage on the surface of the stainless steel products thanks to the function of nitric acid, so that the oxidized layer can be strengthened. In detail, according to the case, an oxidized layer may be caused on the surface of nitrided stainless steel products by the above nitriding treatment. Since this oxidized scale is likely to cause rusts, the corrosion resistance of the nitrided hard layer deteriorates due to the presence of the oxidized scale. Therefore, the oxidized layer can be removed by the above strong mixed acid treatment and prevents the corrosion resistance property from deteriorating. In addition, the corrosion resistance property of austenitic stainless steel is caused by the production of a passive layer (an oxidized layer) based upon the solid solution chrome in the base phase.

The passive layer is produced at the early stage and also strengthened by the above strong mixed acid treatment so that the improvement of corrosion resistance can be seen. As such strong mixed acids, mixed acid containing HNO_3 such as mixed acid composed of HNO_3-HF, mixed acid composed of HNO_3-HCl or the like can be applied. The concentration of HNO_3 of these strong mixed acid should be set at 10 to 20%, 1 to 10% for HF, and 5 to 25% for HCl. Water accounts for the remaining part of strong mixed acid. The above treatment should be performed by dipping the stainless steel products in the above strong mixed acid liquid for 20 to 60 minutes with controlling the liquid temperature of strong mixed acid within 20 to 50 °C. Although the top surface layer occupying 20 to 30% of total nitrided layer is removed by such a strong mixed acid treatment, the surface hardness of remaining parts is still high, wherein the adequate rigidity is maintained. In this case, the nitrided hard layer remained becomes a complete non-magnetic substance by removing the top surface phase. Even though the nitrided hard layer of the top surface layer may have slight magnetic property according to the case, stainless steel products come to show magnetic permeability as same as austenitic stainless steel (base material) because the top surface layer having magnetic property can be removed by the above strong mixed acid treatment. In addition, since the amount of N atoms penetrating into the above top surface layer is great, the above top surface layer may rust more or less compared with the other parts. However, the internal layer, wherein N atoms is relatively few (N atoms: 2 to 5 %), appears to the outside by removing the top surface layer. This layer has adequate hardness, which is only slightly lower than the above top surface layer, and furthermore, has less rusting

characteristic. Therefore, it is suitable for such usage as requires sufficient hardness and complete anti-rust property.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows an EPMA analysis curve chart for samples of EXAMPLES.
Fig. 2 shows an EPMA analysis curve chart for samples of COMPARATIVE EXAMPLES.
Fig. 3 shows an X ray diffraction curve for samples of EXAMPLES.
Fig. 4 shows an X ray diffraction curve for samples of COMPARATIVE EXAMPLES and
Fig. 5 shows a curve of current density and voltage curve.

The following examples and comparative examples are further illustrative of the invention.

EXAMPLE 1

Three kinds of samples (finished by polishing), SUS304 plate (Chrome: 18%, Nickel: 8%), SUS316 plate (Chrome: 18%, Nickel: 12%, Molybdenum: 2%, Core hardness: Hv = 310) and SUS310' plate (Chrome: 25%, Nickel: 20%, Core hardness: HV=370) were prepared. Next, these were charged into a muffle furnace, the inside of the furnace was vacuum purged and raised to 410 °C. Then, maintaining the state, fluoride-containing gas (NF_3 10vol% + N_2 90vol%) was charged into the muffle furnace to form an atmospheric pressure therein and such a condition was maintained for 15 minutes for fluoriding. Then after exhausting the above-mentioned fluoride-containing gas out of the furnace, nitriding gas (NH_3 25vol% + N_2 60vol% + CO 5vol% + CO_2 5vol%) was introduced into the furnace and the inside of the furnace was maintained at 410 °C for 24 hours for nitriding and was withdrawn.

Each surface hardness of the above samples (SUS304 plate, SUS316 plate and SUS310 plate) nitrided in this way was measured. SUS304 plate hardening was Hv of 880, SUS316 plate hardening was Hv of 1050 and SUS310 plate was Hv of 1120. In addition, as for each thickness of the hard layer SUS304 plate was 18 µm, SUS316 plate was 20 µm and SUS310 plate was 18µm.

EXAMPLE 2

The temperature for nitriding of EXAMPLE 1 was changed to 440 °C and the treatment time was changed to 12 hours. The other conditions were the same as EXAMPLE 1. As results of the same measurements for the nitrided products obtained, the each surface hardness for all three was not less than Hv of 1100 and each thickness was 23µm for SUS304 plate, 25 µm for SUS316 plate and 20 µm for SUS310 plate respectively.

EXAMPLE 3

The temperature for nitriding of EXAMPLE 1 was changed to 380 °C and the treatment time was changed to 15 hours. The other conditions were the same as EXAMPLE 1. As results of the same measurements for the nitrided products obtained, the each surface hardness for all three was not less than Hv of 950 and the each thickness was 15 µm for SUS304 plate, 15 µm for SUS316 plate and 12 µm for SUS310 plate respectively.

COMPARATIVE EXAMPLE 1

Three kinds of the same plates as used in EXAMPLE 1 were applied here. Each plate was fluorided at 400 °C and then charged into the same muffle as used in EXAMPLE 1 by using the same gas for nitriding as EXAMPLE 1, and then was nitrided at 550 °C for 5 hours and finally withdrawn. Each surface hardness was Hv of 1280, Hv of 1280 and Hv of 1300 respectively in order, meanwhile each thickness of hard layer was 30 to 35 µm. Next, samples obtained by the above EXAMPLE 1 to 3 were dipped into strong mixed acid liquid containing 5%HF-18%HNO_3 for 60 minutes and then withdrawn for checking. The top surface layer (3 to 6 µm) in the nitrided hard layer of each sample was removed. In addition, as for COMPARATIVE EXAMPLE 1, the same treatment was performed. As a result, a total nitrided hard layer was removed.

Subsequently, surface hardness and content of N atoms in the top surface of nitrided hard layer for each sample obtained from the above EXAMPLE 1 to 3, COMPARATIVE EXAMPLE 1 and those treated by strong mixed acid liquid were worked out. The results are shown in the following Table 1. In the Table 1, "with acid treatment" means that acid treatment was conducted on samples, while "without acid treatment"

means that samples are in the step where the nitriding treatment has finished. In addition, content of N atoms was reckoned by a chart of the results from EPMA analysis done for the each above sample. As regards to corrosion resistance property, time required for rusting was obtained by the results from salt spray tests in accordance with JIS2371 (SST examination).

In addition, whether there is any presence of crystalline chrome was judged from the results of X ray diffraction method for each sample.

TABLE 1

	NITRIDING TEMP. (°C)	ACID TREATMENT	SUS316 (CORE HARDNESS: Hv 310)				SUS310 (CORE HARDNESS: Hv 370)				SUS304 (CORE HARDNESS: Hv 180)			
			SURFACE HARDNESS (Hv)	N CONTENT (WEIGHT %)	CRYSTAL-LINE CHROME	ANTI-CORROSION (SST)	SURFACE HARDNESS (Hv)	N CONTENT (WEIGHT %)	CRYSTAL-LINE CHROME	ANTI-CORROSION (SST)	SURFACE HARDNESS (Hv)	N CONTENT (WEIGHT %)	CRYSTAL-LINE CHROME	ANTI-CORROSION (SST)
EXAMPLE 1	410	WITHOUT	1050	7.6	NONE	NOT LESS THAN 1800h	1120	10.5	NONE	NOT LESS THAN 1800h	1020	7.4	NONE	NOT LESS THAN 1800h
		WITH	820	2.8	NONE	AS SAME AS THE ABOVE	930	5.3	NONE	AS SAME AS THE ABOVE	650	2.5	NONE	AS SAME AS THE ABOVE
EXAMPLE 2	440	WITHOUT	1180	9.0	NONE	48h	1210	11.8	NONE	NOT LESS THAN 48h	1020	8.5	NONE	48h
		WITH	860	5.8	NONE	NOT LESS THAN 1800h	920	7.0	NONE	NOT LESS THAN 1800h	720	4.6	NONE	NOT LESS THAN 1800h
EXAMPLE 3	380	WITHOUT	970	3.7	NONE	AS SAME AS THE ABOVE	960	5.9	NONE	AS SAME AS THE ABOVE	980	3.5	NONE	AS SAME AS THE ABOVE
		WITH	680	1.8	NONE	AS SAME AS THE ABOBE	680	3.2	NONE	AS SAME AS THE ABOVE	600	1.8	NONE	AS SAME AS THE ABOVE
COMPARATIVE EXAMPLE 1	550	WITHOUT	1280	12.8	EXIST	2h	1300	15.6	EXIST	2h	1240	12.6	EXIST	2h
		WITH	330	NOT MORE THAN 0.5	NONE	NOT LESS THAN 1800h	390	0.5	NONE	NOT LESS THAN 1800h	180	NOT MORE THAN 0.5	NONE	NOT LESS THAN 1800h

The following are findings from the above table.

① As clear from comparison of SUS310 of EXAMPLE 2 with acid treatment and SUS316 of COMPARATIVE EXAMPLE 1 without acid treatment, on condition that there is no crystalline chrome nitride in the nitrided hard layer and at the same time concentration of N atoms is limited within 12%, corrosion resistance property can be materialized in the state practically acceptable. Bordering on 12%,

however, when it is over 12%, deposition of crystalline chrome nitride can become seen and as a result corrosion resistance was greatly deteriorated. Conversely, as clear from SUS316 of EXAMPLE 3 with acid treatment, if the concentration of N atoms is lower than 2%, surface hardness usually shows not more than Hv of 700, which is not sufficient as surface rigidity.

② As clear from the comparison among EXAMPLE 1 to 3, and COMPARATIVE EXAMPLE 1, the higher the nitriding temperature is, the more concentration (content) of N atoms in the nitrided hard layer is.

③ When strong mixed acid treatment is conducted, the top surface (wherein the concentration of N atoms is the greatest) of a nitrided hard layer is solved and then removed so that the next internal layer appears, which means the decrease in both concentration of N atoms and surface hardness.

④ From the viewpoint that concentration of N atoms in nitrided hard layer of SU310 is higher than that of SUS316, concentration of N atoms becomes higher in proportion to the concentration of Cr in base material.

⑤ Since crystalline chrome nitride is deposited over whole nitrided hard layer, the sample of COMPARATIVE EXAMPLE lacks corrosion resistance. Therefore, the whole of a hard nitrided layer, which lacks corrosion resistance, disappears and a base material part is revealed.

Besides, the results of the above EPMA analysis are shown in Fig. 1 (EXAMPLE 1) and Fig. 2 (COMPARATIVE EXAMPLE 2) taking EXAMPLE 1 (SUS316 without acid treatment) and COMPARATIVE EXAMPLE 1 (SUS316 without acid treatment) as representatives. As clear from the curves of N atom concentration in Fig. 1 and Fig. 2, N atom concentration (content) in the top surface of the nitrided hard layer in EXAMPLE 1 (SUS316) is 7.6% by weight, meanwhile that in COMPARATIVE EXAMPLE 1 (SUS316) is 12.8% by weight, which is remarkably high. The concentration of N atoms in the above EPMA is measured by a basic measurement line.

Furthermore, the results of X-ray diffraction method for the above EXAMPLE 1 and the COMPARATIVE EXAMPLE 1 (both are SUS316 without acid treatment) are shown in Fig. 3 (EXAMPLE 1) and Fig. 4 (COMPARATIVE EXAMPLE 1) as representative. In these figures, curve (I) represents an X-ray diffraction method of EXAMPLE 1, curve (II) an X-ray diffraction method of SUS316 (SUS316 materials without nitriding treatment) and curve (III) an X-ray diffraction method of COMPARATIVE EXAMPLE 1. In Fig. 3, γ n represents γ phase (base phase) containing N atoms by nitriding. In comparison of curve (I) and (II), γ n phase (base phase) of curve (I) is slipped against the left side (low angle side) of γ -Fe phase (base phase) of corresponding curve (II), wherein lattice is distorted by an increase of lattice constant, so that surface hardness in samples of EXAMPLES can be improved. On the other hand, in curve (III) of COMPARATIVE EXAMPLES, plenty of crystalline chrome nitride peaks such as CrN can be seen, which decreases corrosion resistance of this nitrided layer.

Still furthermore, to check corrosion resistance electrochemically, each sample of EXAMPLE 1 and COMPARATIVE EXAMPLE 1 (each of them is SUS316 without acid treatment) obtained in the above method was given anodic polarization test (in accordance with JIS G 0579). The results are shown in Fig. 5. Checking the current electric level in vicinity of a passive range (a broken line X), it is found out that EXAMPLE 1 (curve A) does not deteriorate so much compared with SUS316 base material (curve B) in which nitriding treatment was not conducted. On the other hand, it is found out that difference between COMPARATIVE EXAMPLE 1 (curve C) and SUS316 base material (curve B) is not less than a number of three figures, which means that the corrosion resistance has greatly deteriorated due to nitriding treatment.

EXAMPLE 4

Socket screws (M6) formed by cold forging from each wire rod made of SUS304 (chrome: 18%, nickel: 9%), SUS316 (Chrome: 18%, nickel: 12%, molybdenum: 2.5%), SUS310 (chrome: 25%, nickel: 20%) and a hardened SUS309 material (chrome: 22%, nickel: 12%) by work hardening were subjected to fluoriding and nitriding treatment under the same procedure and conditions as same as EXAMPLE 1. Each surface hardness of nitrided samples was Hv of 1100 to 1150 and the depth of the whole nitrided hard layer was 18 to 20 µm. Next, these were subjected to shot blast so as to remove the oxidized scale attached thereon and then subjected to SST examination. Each rusted within 72 hours.

Next, these samples were dipped into strong mixed acid liquid of 20%HCl-13%HNO_3 at the temperature of 45 °C for 60 minutes. Measuring the hardness, each surface hardness of them are Hv of 850 to 900, while each thickness of hard nitrided layer was reduced by strong mixed acid by 5 to 8 µm to 12 to 15 µm. And then, the above samples after acid treatment were subjected to SST examination. As a result, corrosion resistance was improved and each of them did not rust at all over 1800 hours.

EXAMPLE 5

Non-magnetic stainless steel bar (chrome: 18%, nickel: 12%, Mn: 1.5%), to which a small amount of N atoms were added by steel-making process, and SUS316 bar were fluorided and nitrided in the same procedure and conditions as EXAMPLE 1. Next, nitrided articles obtained was dipped into strong mixed acid liquid of 10%HF-15%HNO_3 at the temperature of 40 °C for 30 minutes and finally withdrawn.

Next, each magnetic permeability (μ) of these was measured. It is found out that each of them does not have magnetism by nitriding treatment as follows:

	Non-magnetic stainless bar		SUS316 bar	
	magnetic permeability (μ)	surface hardness (Hv)	magnetic permeability (μ)	surface hardness (Hv)
before nitriding	1.001	480	1.002	240
after nitriding	1.015	1210	1.050	1120
after acid cleaning	1.001	990	1.002	920

EFFECT OF THE INVENTION

As aforementioned, since nitrided stainless steel product in the present invention contains substantially no crystalline chrome nitride in the nitrided hard layer forming the surface layer, solid soluble chrome in austenitic stainless steel (base phase) is not consumed by deposition of crystalline chrome nitride, compared with nitrided stainless steel products containing crystalline chrome nitride in its nitrided hard layer. Therefore, passive layer coat (oxidized coat), which is formed by the function of crystalline chrome in the base phase, can be produced enough, so that it becomes to have excellent corrosion property as same as that of the above base phase. In addition, since substantially no rough crystalline chrome nitride is produced in the nitrided hard layer by deposition, dimensional change or surface roughness of nitrided stainless steel products is not deteriorated by deposition of crystalline chrome nitride. As a result, there is no need to perform a final finishing process after nitriding treatment. And then, stainless steel products in the present invention can have the same excellent hardness as those formed by nitrided hard layer made of crystalline chrome nitride because said stainless steel products contain N atoms at 2 to 12% in the base phase of the surface layer, which has penetrated thereto.

Claims

1. Nitrided stainless steel comprising austenitic stainless steel, wherein a portion of the surface layer at least is composed of a nitrided hard layer which:
   (A) contains substantially no crystalline chrome nitride;
   (B) contains 2 to 12% by weight N atoms in austenitic stainless steel phase of base phase.

2. Stainless steel according to claim 1 containing not less than 22% by weight chrome.

3. Stainless steel according to claim 1 or 2 containing not less than 1.5% by weight molybdenum.

4. Stainless steel according to any preceding claim wherein the nitrided hard layer contains at 2 to 5% by weight N atoms.

5. A product comprising nitrided stainless steel according to any preceding claim.

FIG. 1

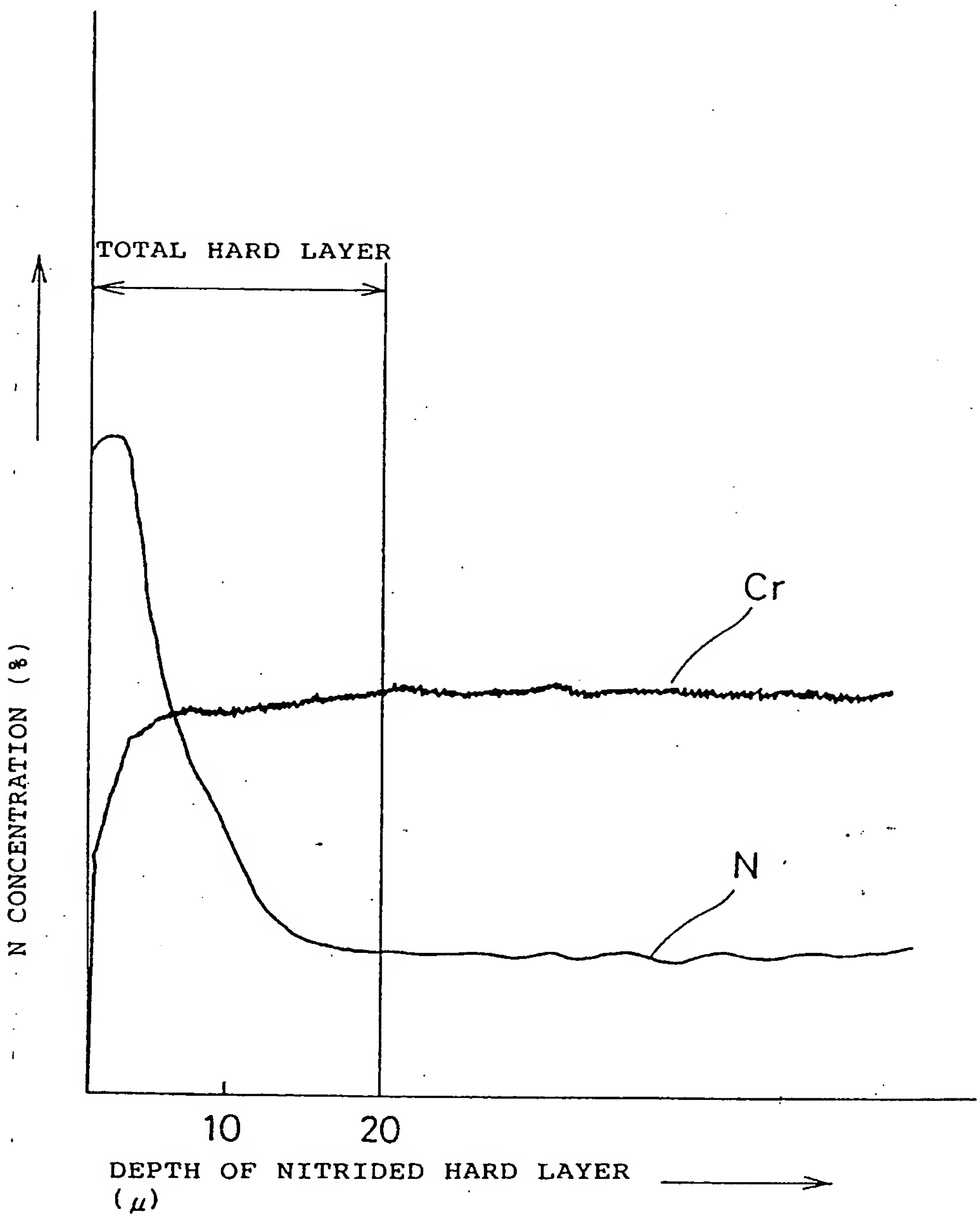

TOTAL HARD LAYER
N CONCENTRATION (%)
Cr
N
10
20
DEPTH OF NITRIDED HARD LAYER
(μ)

FIG. 2

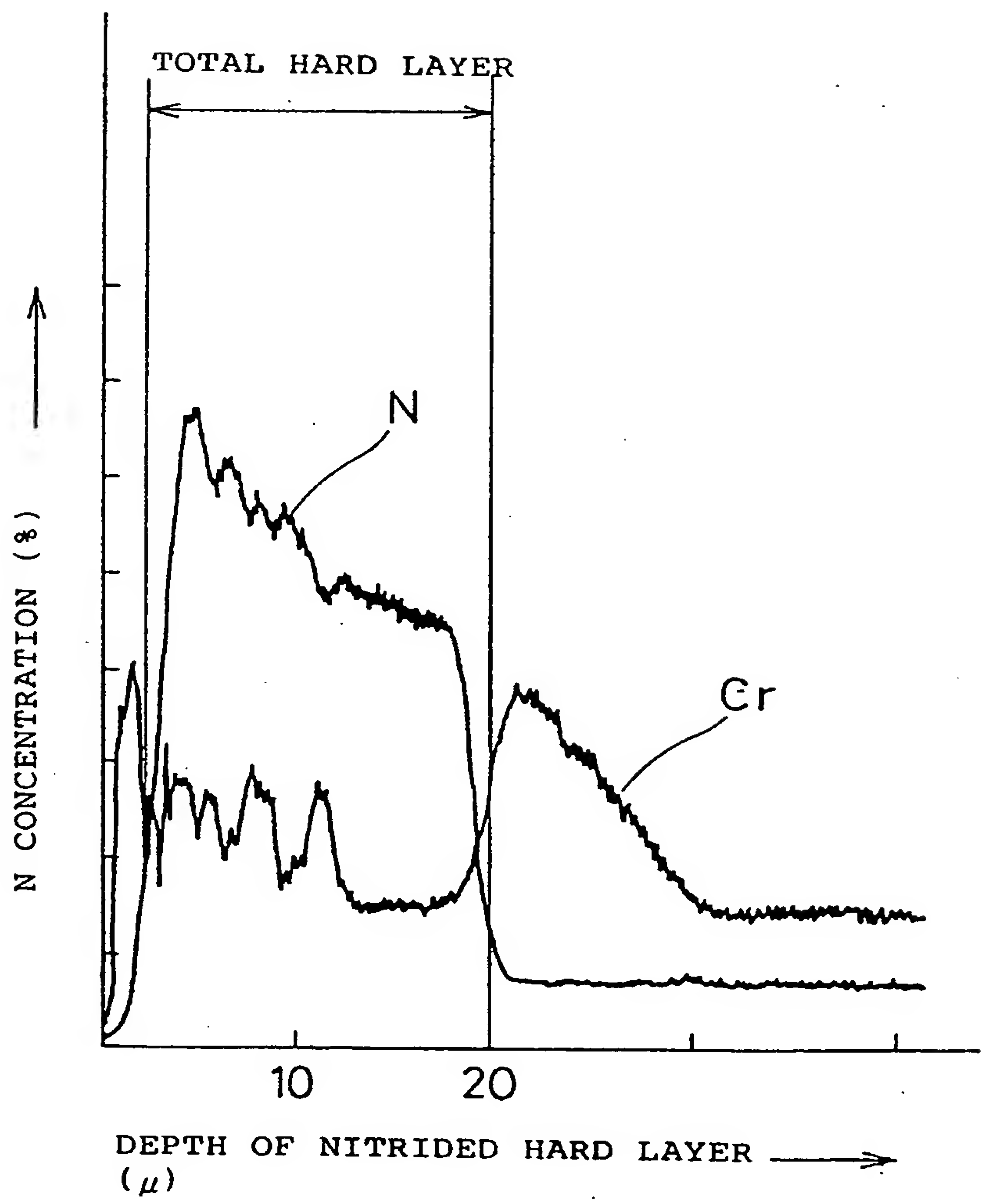

TOTAL HARD LAYER
N
Cr
N CONCENTRATION (%)
10
20
DEPTH OF NITRIDED HARD LAYER
(μ)

FIG. 3

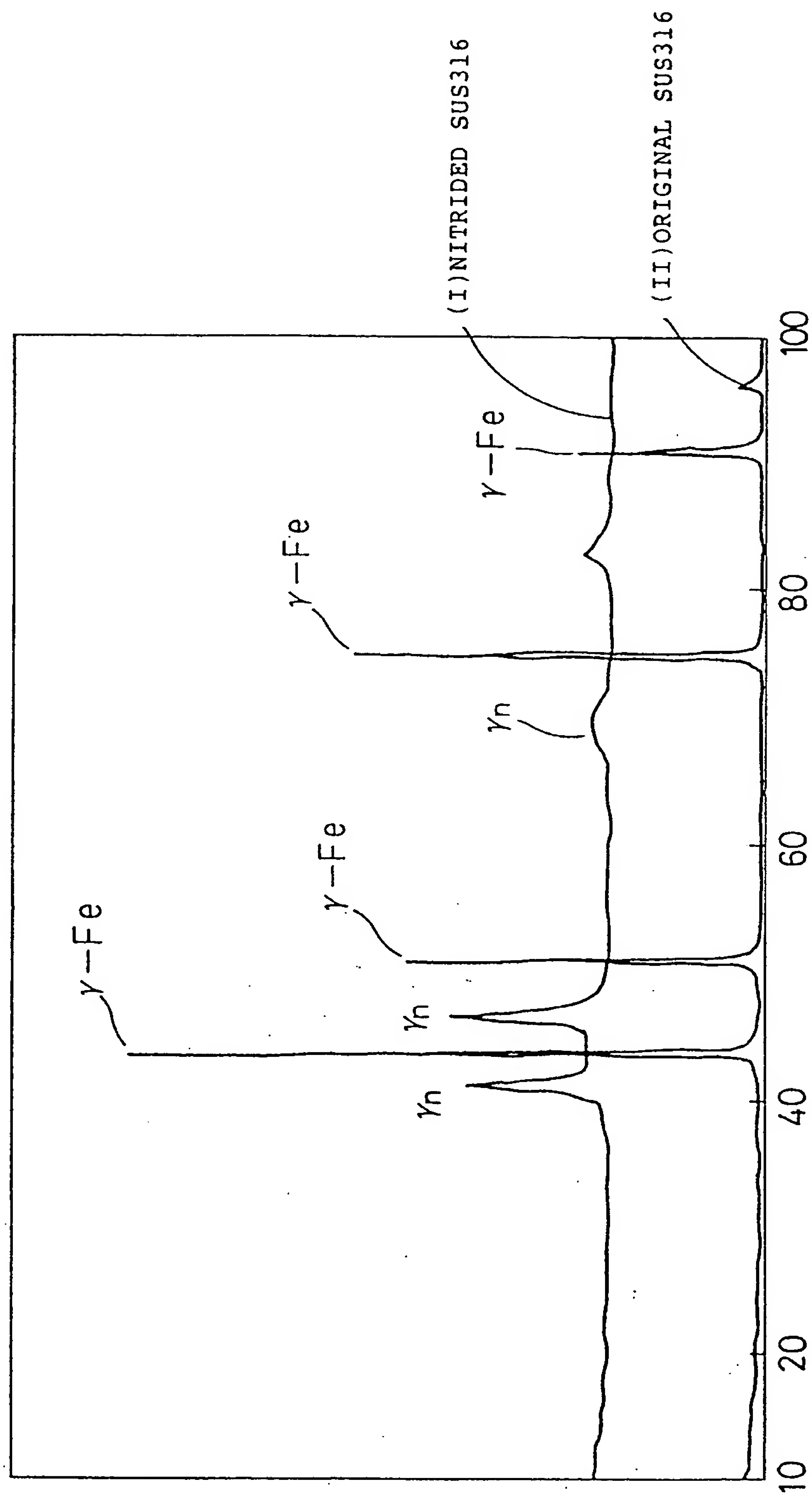

(I)NITRIDED SUS316
(II)ORIGINAL SUS316
γ—Fe
γ—Fe
γ—Fe
γ—Fe
γn
γn
γn
10
20
40
60
80
100

FIG.4

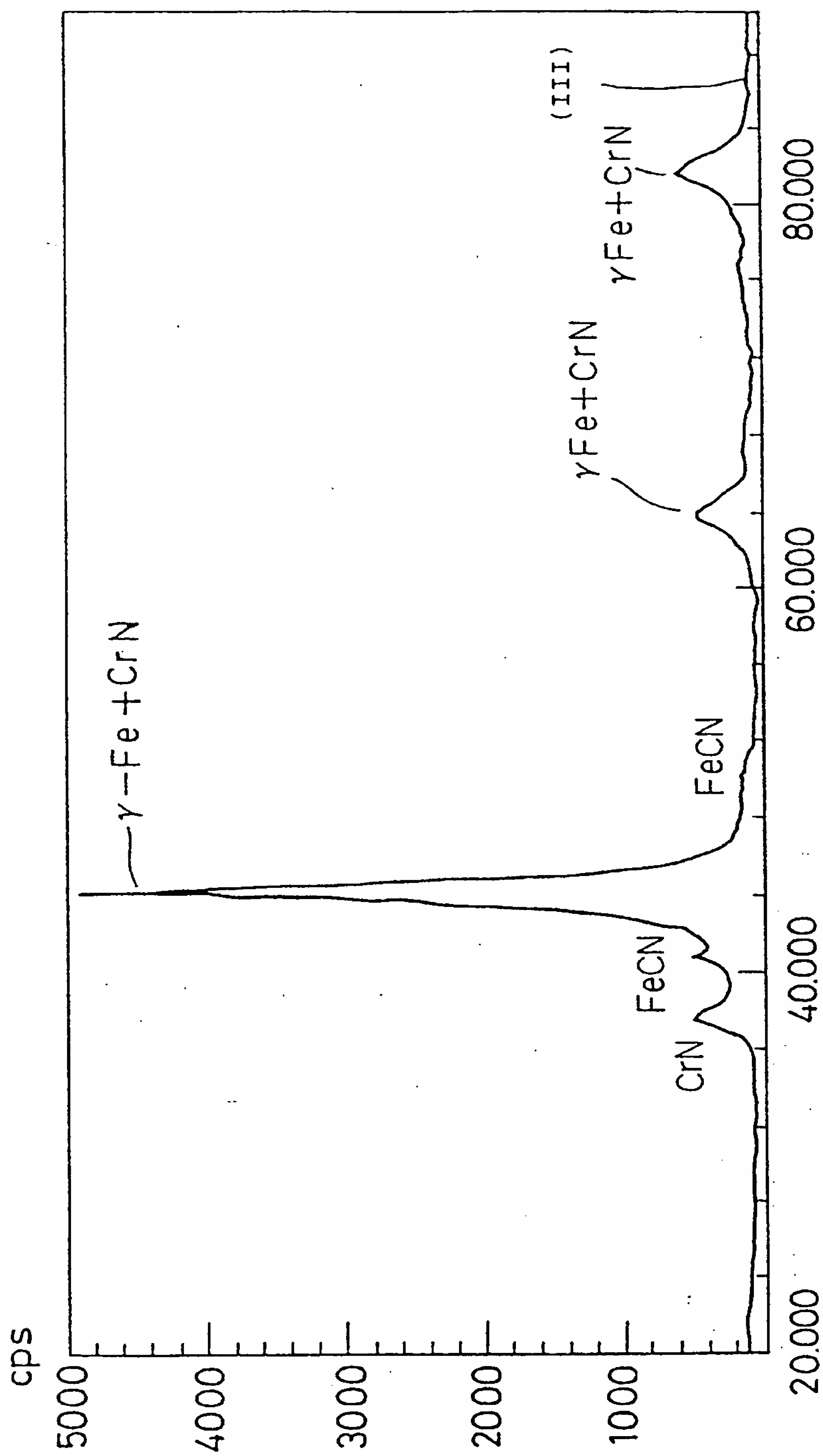
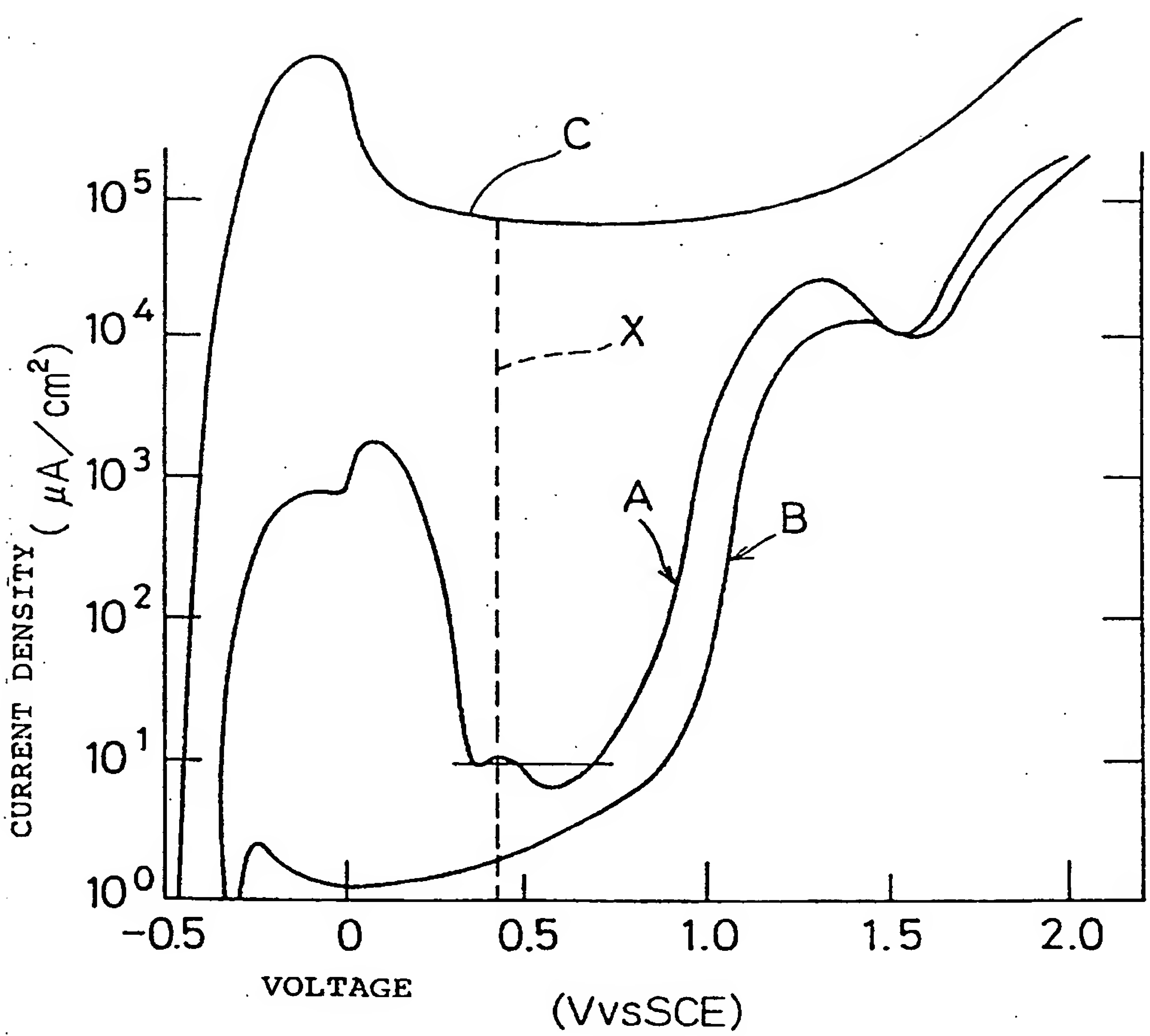

cps
5000
4000
3000
2000
1000
20.000
40.000
60.000
80.000
γ−Fe+CrN
CrN
FeCN
FeCN
γFe+CrN
γFe+CrN
(III)

FIG. 5


C
X
A
B
10^5
10^4
10^3
10^2
10^1
10^0
CURRENT DENSITY (μA/cm²)
−0.5
0
0.5
1.0
1.5
2.0
VOLTAGE
(VvsSCE)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 93302930.8

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP - A - 0 408 168 (DAIDOUSANSO CO., LTD.) * Abstract; claims 1-17 * --	1-5	C 23 C 8/26 C 23 C 8/02
A	EP - A - 0 511 409 (DAIDOUSANSO CO., LTD.) * Abstract; fig.1; claims 1-2 * --	1-5	
A	EP - A - 0 515 701 (DAIDOUSANSO CO., LTD.) * Abstract; fig. 1; claims 1-2 * ----	1-5	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C 23 C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	06-05-1994	HAUK

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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